

PATENT SPECIFICATION 738,808



Date of Application and filing Complete Specification : Aug. 10, 1953.

No. 22053/53.

Application made in United States of America on Sept. 10, 1952.

Complete Specification Published : Oct. 19, 1955.

Index at Acceptance :—Class 2(3), C3A10B2, C3A13A3 (A2:B2:G), C3A14A (2A:7B).

COMPLETE SPECIFICATION

A method for the oxidation of cycloalkanes

We, ESSO RESEARCH AND ENGINEERING COMPANY, formerly known as STANDARD OIL DEVELOPMENT COMPANY, a corporation duly organised and existing under the laws of the State of Delaware, United States of America, having an office at Elizabeth, New Jersey, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to a novel process for oxidizing cycloalkanes with a free oxygen-containing gas.

Processes have been previously proposed for oxidation of cycloalkanes such as cyclohexane through the utilization of gaseous oxygen. In one of these, cyclohexane is oxidized by air in a first step to produce an oxidation oil comprising adipic acid and numerous other oxy-compounds some of which are intermediate in nature. The oxidation oil is, therefore, separated from unreacted cyclohexane and oxidized in a second step by the use of nitric acid to produce substantially increased yields of adipic acid. While this process gives satisfactory overall yields, it suffers from the disadvantage that costly nitric acid is consumed. In order to make this process commercially feasible it is necessary to recover the nitrogen oxides produced and to regenerate nitric acid. Unless facilities for this purpose are available, this expedient requires considerable additional capital expenditure and specialized operating "know how." Thus, the attractiveness of this adipic acid process depends primarily on the availability of a nitric acid regeneration plant.

In another adipic acid process, cyclohexane is admixed with a substantial proportion of acetic acid which serves as a

solvent or diluent and air oxidation of the 45 cyclohexane to adipic acid is effected in one stage. Unconverted cyclohexane, acetic acid and neutral oxygenated compounds are recovered and recycled with fresh feed. This process avoids the use of costly nitric acid, but, on the other hand, does not produce as high yields of adipic acid as the above two-stage process. In addition, the presence of acetic acid and the necessity for its recovery and recycling greatly complicate the required 55 processing facilities.

It has now been found that oxidizing cycloalkanes with oxygen-containing gases to oxy compounds, i.e. acids, ketones, and alcohols, can be accomplished in the absence 60 of extraneous solvent, in a manner which completely overcomes the disadvantages of the prior art by utilizing the process of this invention. The present process comprises, in effect, the steps of subjecting a cycloalkane containing at least four cyclic carbon atoms to oxidation by means of a free oxygen-containing gas, at a temperature of 65 from 100 to 200°C. and at pressure at least sufficient to maintain the cycloalkane in the liquid phase, separating the resultant reaction mixture into an upper liquid hydrocarbon-rich phase and a lower phase rich in oxy compounds containing water and some dissolved hydrocarbons, distilling the 75 liquid oxy compound-rich phase so as to remove hydrocarbons and water therefrom, withdrawing the residual material containing the oxy compounds from which the water and hydrocarbons have been removed from 80 the distillation step; and further oxidizing this residual material by means of a free oxygen-containing gas at a temperature of from 100 to 170°C. and at a pressure at least sufficient to maintain the residual 85 material in the liquid phase.

In this manner it is possible to oxidize saturated cyclic hydrocarbons containing at least 4 cyclic carbon atoms, such as cyclo-

Price 4s. 6d.

Price 3s. 6d.

Price 5s. 0d.

hexane, cyclopentane and cyclobutane or homologs such as the methyl-, dimethyl-, ethyl-substituted cyclic hydrocarbons or their homologs, with the production of the corresponding dibasic acids such as glutaric or succinic acid or their homologs. This process is particularly useful in the oxidation of cyclohexane because of the utility of the adipic acid, cyclohexanol, and cyclohexanone products.

Preferably the first stage oxidation is carried out at temperatures in the range of 115°C. to 150°C., while the second stage oxidation is preferably carried out at temperatures in the range of 100 to 130°C. Pressures ranging from about 2 to about 100 atmospheres or higher can be used. Pressures of 5 to 25 atmospheres are preferred. The minimum pressure is that required to permit effecting the reaction in the liquid phase, by which is meant that the hydrocarbon is oxidized in the liquid state. Pressures in excess of this minimum may be used, however, since pressure has been found to favor the reaction rate.

Catalysts may be employed, but their use is not critical. Conventional catalysts known in the art include polyvalent metals having an atomic weight between 50 and 200. Such metals may be used in the finely divided state or as organic and inorganic salts or oxides. Specific metals include, for example, cerium, cobalt, copper, manganese, and uranium. As specific catalysts under the above description there may be employed vanadium, cerium and cobalt chlorides, manganese naphthenate, manganese acetate alone or together with barium acetate, barium or cobalt permanganate, sodium cobaltinitrite or mixtures of two or more of such compounds. In addition to the oxidation catalysts, promoters such as the salts of alkali and alkaline earth metals may also be employed, if desired, such, for example, as the barium, magnesium and potassium acetates, butyrates and propionates.

This invention will be better understood by reference to the flow diagram shown in the accompanying drawing.

Preheated liquid cyclohexane is fed through line 1 into oxidation tower 2. Air enters oxidation tower 2 through line 3. The temperature in oxidation tower 2 is maintained at about 130°C. Spent air together with entrained cyclohexane vapors and water is taken overhead through line 5 and cooled in heat exchanger 6. The condensate of cyclohexane and water thus obtained is sent from heat exchanger 6 through line 8 to separator 14. Spent air is vented through line 7. The reaction product is drawn off from oxidation tower 2 through line 4, cooled in chiller 29, and filtered on rotary filter 30. Solid adipic acid is collected in

hopper 31 and filtrate fed to separator 9 through line 32. In separator 9 a phase separation takes place into a lighter, hydrocarbon-rich upper phase and a heavier, oxy compound-rich lower phase. The hydrocarbon-rich layer is recycled through lines 10 and 33 to line 1 where it is combined with fresh feed and introduced in oxidation tower 2. The oxy compound-rich lower phase is drawn off through line 11 to stripper tower 12, in which physically dissolved cyclohexane and water are distilled overhead through line 13. The distillation is conducted at a temperature such that the hydrocarbon, i.e., cyclohexane, and water are completely removed through line 13. The temperature in this case is about 82°-87°C. In separator 14 water is removed as the lower layer through line 15, and hydrocarbon is recycled through lines 33 and 1 to oxidation tower 2. The water layer leaving separator 14 by line 15 may be discarded or processed for the recovery of water-soluble degradation products as desired. The bottoms from distillation tower 12 are removed through line 16 to oxidation tower 17. This bottoms layer, from which the hydrocarbon and water have been removed, contains substantially only the intermediate oxy compounds. These oxy compounds are further oxidized in oxidation tower 17 with air introduced through line 19 at a temperature of 115°C. The oxidation product from tower 17 is removed through line 18 and combined with reactor product from oxidation tower 2 in line 4. The combined reaction products are cooled in chiller 29 and the adipic acid filtered as before.

A purge line 20 is provided to prevent excessive buildup of light, water-insoluble oxy compounds. Similarly, a portion of the oxidation reaction product from oxidation tower 17 may be purged through line 21 to prevent excessive buildup of lactones, monobasic fatty acids, and other oxidation-resistant condensation products. If it is desired to recover some of the intermediate oxidation products such as cyclohexanol, they may be conveniently recovered from line 16. Undesired or deleterious higher boiling oxidation by-products may be purged also from line 16 as shown.

It may be preferred under certain conditions of conversion and selectivity to operate tower 12 in the presence of excess water introduced through a separate line (not shown). This would permit complete recovery of dissolved cyclohexane as an overhead azeotropic fraction at a temperature of 68°-70°C.

This invention will be better understood by reference to the following example of the preparation of the indicated products according to the process of this invention.

EXAMPLE

A series of seven batch oxidation runs was carried out wherein air at 150 psig was blown through cyclohexane at 150°C. at the rate of approximately 300 vols. air per vol. liquid cyclohexane per hour. The liquid-solid effluent from each run was separated mechanically into a hydrocarbon-rich upper layer and an oxy-compound-rich slurry (oxidation oil and solid acids). The hydrocarbon-rich layer was recycled with makeup to the oxidation vessel. This operation was repeated a total of seven times.

The oxy-compound-rich slurries from the final four runs were composited, chilled and filtered to remove the bulk of the adipic acid produced and the remaining acid-lean oil (filtrate) was in turn passed to the second stage oxidation vessel after topping to remove the small amounts of dissolved cyclohexane and water. After subjecting the acid-lean oil to oxidation for a period of one hour at 120°C. and 150 psig air pressure (air rate, approximately 300 v./v./liq./hour) it was found that the crude adipic acid content of the acid-lean oil had increased 41 per cent representing an increase of 29 per cent on the initial yield of adipic acid. The overall selectivity to adipic acid was correspondingly increased from 17 mole per cent (first stage) to 22 mole per cent (first stage + second stage oxidation).

These figures demonstrate how a 1/3 increase in yield of adipic acid was obtained utilizing the two-stage oxidation features of this invention.

The oxidation products derived from any of the various cycloalkanes may be further purified by procedures known to the art. Such purification is not a part of this invention and need not be elaborated upon herein.

There are several distinct advantages inherent in the process of this invention. Among these are the simplicity and effi-

ciency of the process, e.g., the reactor effluent separates readily into two liquid phases, the lighter of which is suitable for recycle without further processing. This makes the process ideally adapted for continuous operation. The increased yields obtained and the ease of separation of products are other distinct advantages.

What we claim is:—

1. A method of oxidizing cycloalkanes which comprises the steps of subjecting a cycloalkane containing at least four cyclic carbon atoms to oxidation by means of a free oxygen-containing gas at a temperature of from 100 to 200°C. and at pressure at least sufficient to maintain the cycloalkane in the liquid phase, separating the resultant reaction mixture into an upper liquid hydrocarbon-rich phase and a lower phase rich in oxy compounds containing water and some dissolved hydrocarbons, distilling the liquid oxy compound-rich phase so as to remove hydrocarbons and water therefrom, withdrawing the residual material containing the oxy compounds from which the water and hydrocarbons have been removed from the distillation step; and further oxidizing this residual material by means of a free oxygen-containing gas at a temperature of from 100 to 170°C. and at a pressure at least sufficient to maintain the residual material in the liquid phase.

2. A process according to Claim 1, in which the cycloalkane is cyclohexane, and the desired oxidation product is adipic acid.

3. A process according to Claim 2, including the additional step of removing solid adipic acid from the process reaction mixture prior to the separation step.

D. YOUNG and CO.
29, Southampton Buildings,
Chancery Lane, London, W.C.2.
Agents for the Applicants.

738,808 COMPLETE SPECIFICATION

1 SHEET

This drawing is a reproduction of
the Original on a reduced scale.

PUBLISHED BY :
THE PATENT OFFICE,
25, SOUTHAMPTON BUILDINGS,
LONDON, W.C.2.

